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KINETIC STUDIES FOR XeF AND KrF LASERS

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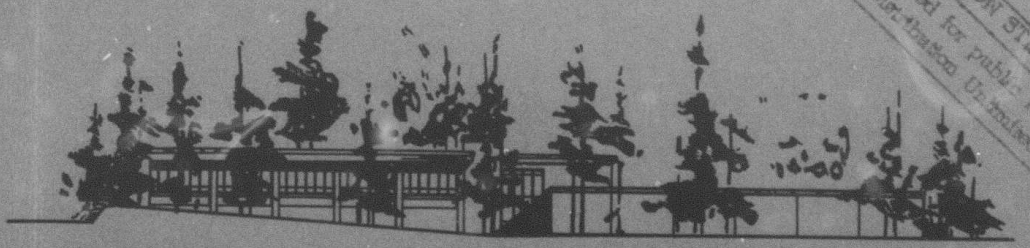

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I. INTRODUCTION

The goal of this program is to determine the radiative lifetime and the collisional quenching rate coefficients for the XeF and KrF upper laser levels using a state selective, laser excited fluorescence technique. Details of the experimental procedure were described in our semi-annual report.[1] During this reporting period, we have determined the XeF($B^1/_2$) radiative lifetime by monitoring the decay of the 353 nm XeF($B^1/_2 \rightarrow X$) fluorescence as a function of pressure. Preliminary collisional quenching rate constants have been determined for He, Xe, and F_2 from the variation of the fluorescence decay time constant as a function of partial pressure of the collision partner. Collisional quenching by Ar was investigated; however, no bimolecular rate constant was determined because of nonexponential decay of the XeF($B \rightarrow X$) emission in the presence of Ar. This behavior suggests collisional coupling to some other excited state, most likely the XeF($C^3/_2$) state.

Bimolecular collisional quenching rate coefficients by Ne and NF_3 remain to be determined during the next reporting period. In addition, termolecular quenching by He, Ne, and Ar will be investigated by increasing the partial pressures of these constituents to the 1 to 3 atm range. Collisional coupling between the $B^1/_2$ and $C^3/_2$ states will also be investigated by looking for fluorescence at 460 nm on the XeF($C \rightarrow X$) band.

II. EXPERIMENTAL RESULTS

2.1. XeF(B ½) Radiative Lifetime

Oscilloscope traces showing the 351 nm exciting pulse and the 353 nm fluorescence signal are presented in Figure 1. This signal was obtained with a He + 10 torr Xe +0.7 torr UF_6 gas mixture at 125 torr total pressure. We have switched to UF_6 as the F atom source because its UV absorption cross section (resulting in dissociation to produce an F atom) is two orders of magnitude larger than that of F_2, which yields a substantial increase in the XeF fluorescence. However, the UF_5 produced during the flash has a low vapor pressure resulting in the formation of solid particles which increased the scattered light from the 351 nm exciting pulse on subsequent shots. Therefore, it was necessary to pump out the cell and refill it with fresh gas after every shot.

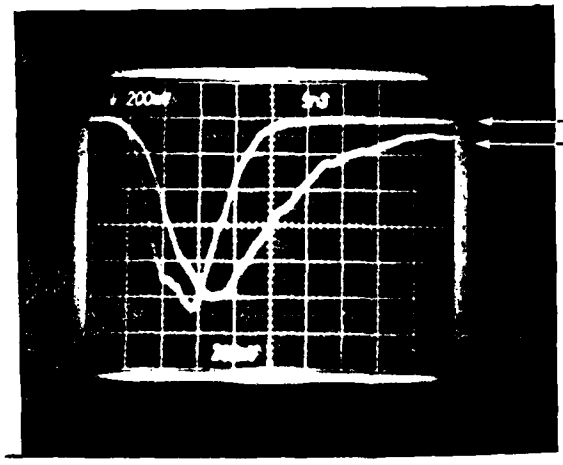
If the XeF(B ½) excited state is lost only by radiative decay and bimolecular collisions, it will decay exponentially once the exciting laser pulse has terminated. A semilogarithmic plot of the 353 nm fluorescence decay read from the oscilloscope trace is presented in Figure 1. The slope of the straight line fit to the data yields the decay time constant τ^{-1} given by

$$\tau^{-1} = \tau_B^{-1} + k_{He}[He] + k_{Xe}[Xe] + k_{UF_6}[UF_6]$$

$$= \tau_B^{-1} + (k_{He}X_{He} + k_{Xe}X_{Xe} + k_{UF_6}X_{UF_6})\, p$$

where τ_B is the radiative lifetime of the XeF(B ½) state, k_i and X_i are the quenching rate coefficient and the mole fraction of the ith component of the mixture, and p is the total pressure. Thus, a plot of the decay time constant τ^{-1} as a function of pressure for a

a)



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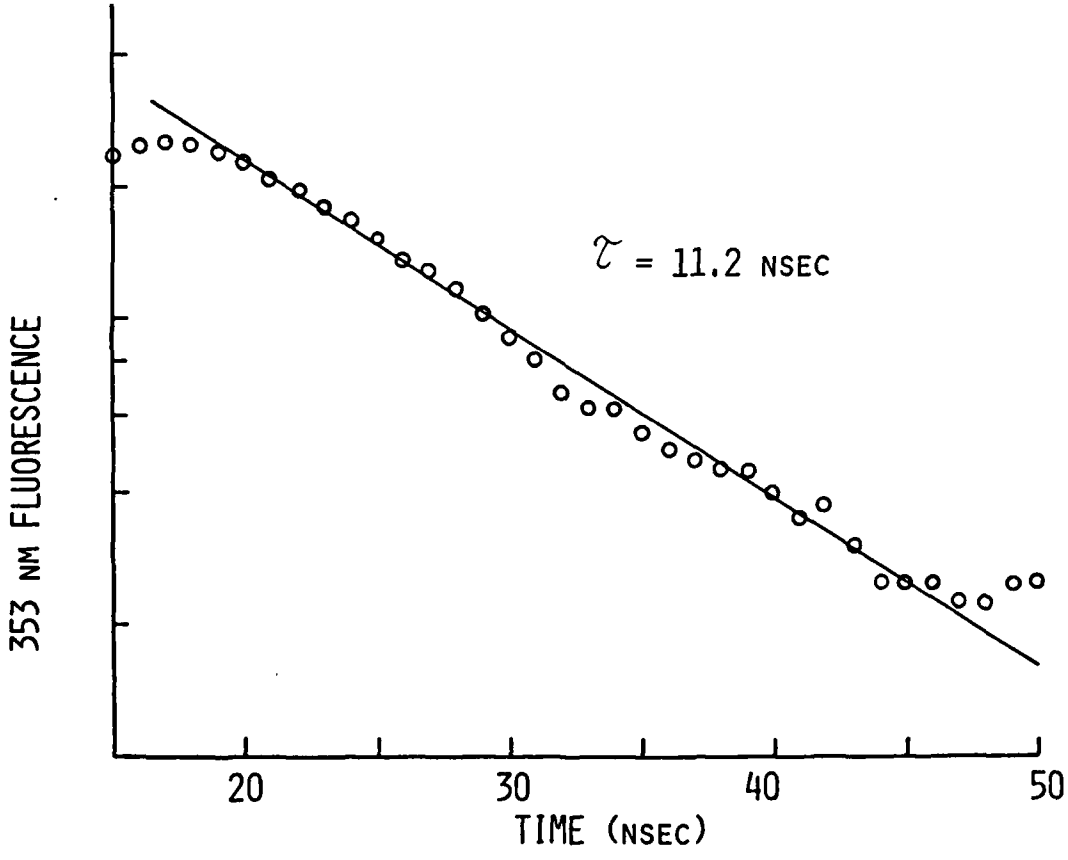

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Figure 1. The 353 nm Fluorescence from a Gas Mixture of He+10 Torr Xe + 0.7 torr UF_6 at a Total Pressure of 125 torr. a) Oscilloscope traces showing the 351 nm exciting laser pulse and the 353 nm fluorescence signal. b) Semi-logarithmic plot of the 353 nm fluorescence decay.

gas mixture with fixed composition should follow a straight line with the XeF(B ½) radiative lifetime as the zero pressure intercept. A plot of the data obtained for a He + 4% Xe + 0.13% UF_6 gas mixture is shown in Figure 2. The zero pressure intercept of the straight line fit to the data gives a XeF(B ½) radiative lifetime of 18.7 ± 1.4 nsec. This result is in good agreement with that obtained by Burnham and Harris from the dissociative excitation of XeF_2.[2]

2.2. XeF(B ½) Collisional Quenching

Bimolecular quenching rate constants for various molecules are obtained by measuring the XeF (B ½) decay time constant as a function of the partial pressure of that constituent while holding the partial pressures of the other constituents fixed. The slope of the straight line fit to the data gives the two-body quenching rate constant for that molecule. To illustrate the procedure, a plot of the 353 nm decay time constant τ^{-1} as a function of F_2 partial pressure is shown in Figure 3. The partial pressures of the other constituents of the gas mixtures were held fixed at 250 torr He + 10 torr Xe + 0.3 torr UF_6. The quenching rate constant for F_2 determined from the slope of the straight line fit to the data is $k_{F_2} = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}. Using this same procedure, quenching rate constants for He and Xe have also been determined. These rate constants are listed in Table 1 along with the pressure range over which the quenching was studied. The measured rate constants are in fairly good agreement with those inferred by Brashears, Setser and Desmarteau from Stern-Volmer plots of the quenching of XeF(B ½ → X) emission produced by photolysis of XeF_2.[3]

No quenching rate constant is listed in the table for Ar even though it is a primary constituent of e-beam excited XeF laser

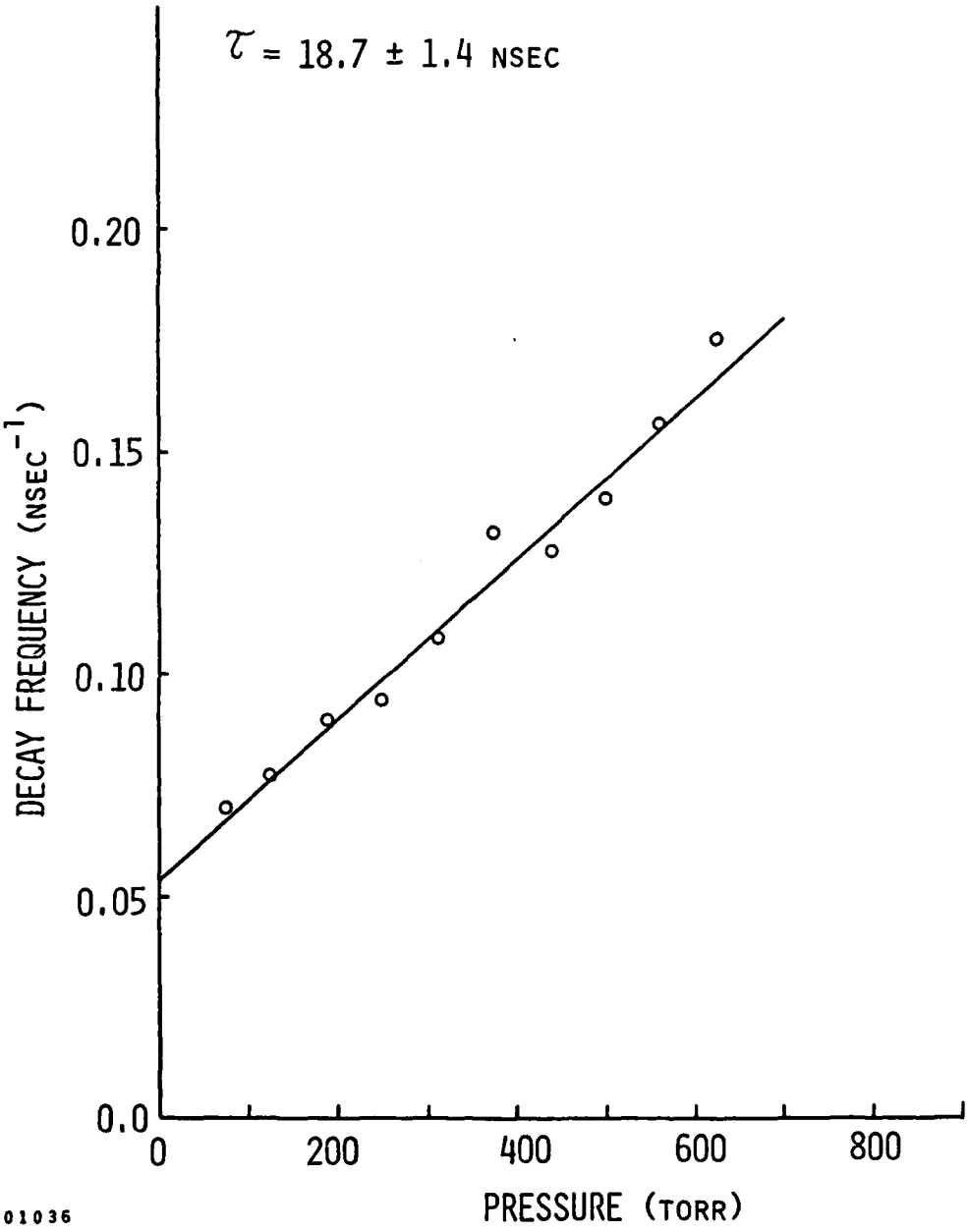

Figure 2. Decay Frequency as a Function of Pressure for a He + 4% Xe + 0.13% UF_6 Gas Mixture. The zero pressure intercept of the straight line fit to the data gives a XeF (B^1_2) radiative lifetime of 18.7 nsec.

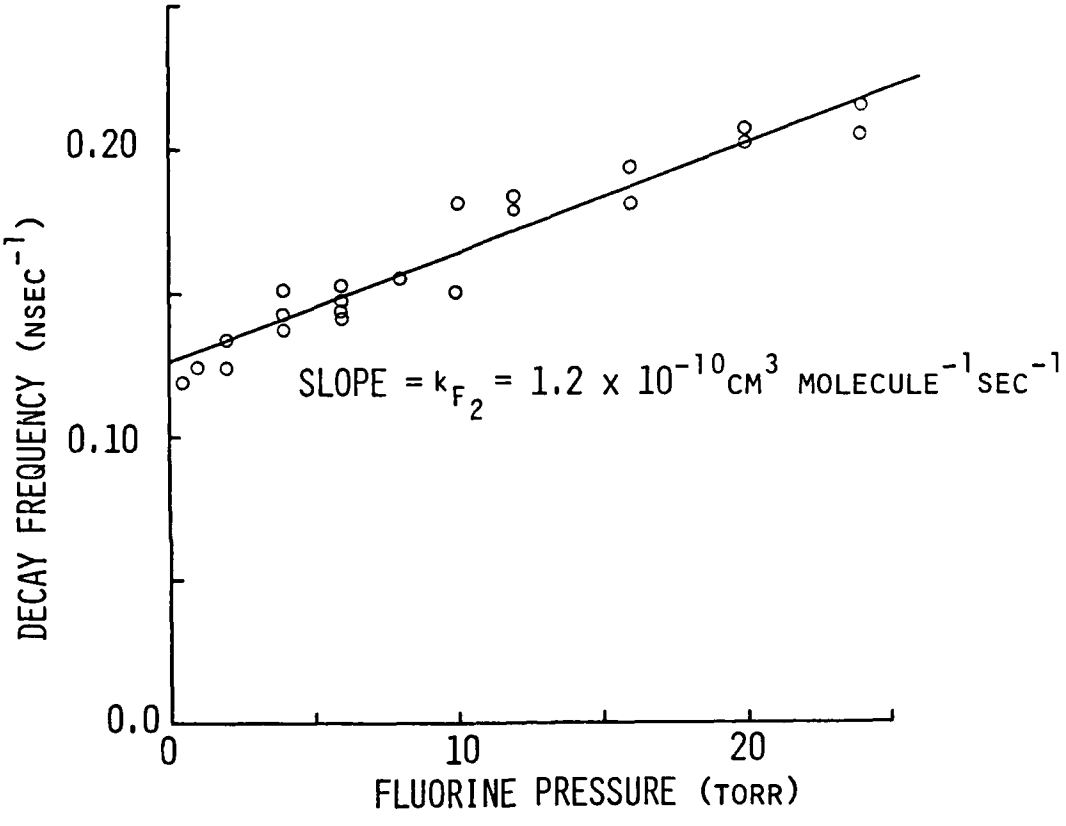

Figure 3. Variation of 353 nm Fluorescence Decay as a Function of Fluorine Partial Pressure. The slope of the straight line fit to the data gives a quenching rate constant of 1.2 x 10^{-10} cm^3 molecule^{-1} sec^{-1}.

Table 1

Summary of XeF (B ½) Radiative Lifetime
and Quenching Data

XeF(B ½) τ_r = 18.7 ± 1.4 nsec
XeF(B ½) 2-Body Quenching Rate Constants

Molecule	k_q(cm^3 Molecule^{-1} sec^{-1})	Pressure Range (torr)
He	2×10^{-12}	75 - 750
Xe	6×10^{-11}	5 - 80
F_2	1.2×10^{-10}	0.5 - 24

mixtures. This is due to the fact that the 353 nm fluorescence in the presence of Ar exhibited nonexponential decay over much of the pressure range studied, making it difficult to extract a rate constant without a more complicated analysis. This behavior suggests collisional transfer from the $B^1/_2$ state during the decay period. The most likely candidate is the $XeF(C^3/_2)$ state which is nearly degenerate with the $B^1/_2$ state.[4] During the next reporting period, the possibility of collisional coupling between the $B^1/_2$ and $C^3/_2$ states will be investigated by looking for broadband fluorescence at 460 nm on the $XeF(C^3/_2 \rightarrow X)$ transition.

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